

Nanopatterned Photo-responsive Hydrogels

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Motivation

Nanopatterned Hydrogels have enabled:

- Fabrication of combinatorial arrays
- Nanoscale sensors
- Micro- or nanofluidic devices
- Tissue engineering applications

Stimuli-responsive Hydrogels

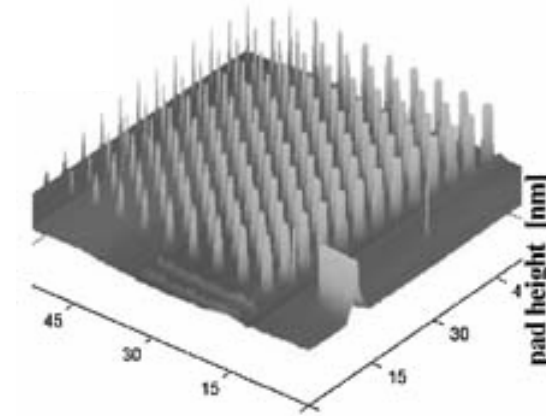
- Difficult to control
- Exponential complexity with increased-scale
- Required stimuli reduces application
- Current light-stimuli hydrogels are micron-scale

E-beam patterned bacteriorhodopsin-containing hydrogels

- Nanopatterned hydrogels are responsive to visible green-light
- Response depends on electron-dose and ionic strength
- Response is repeatable under cyclic light/dark exposure

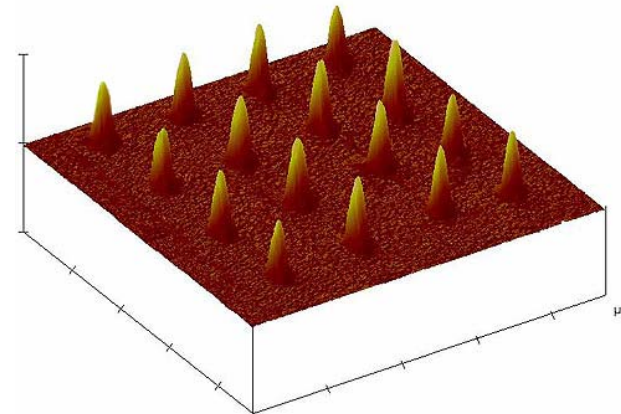
Can we make photo-responsive nanopatterned hydrogels comparable to current stimuli-responsive nanopatterned hydrogels?

Current thermally-responsive
nanopatterned hydrogels



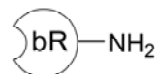
Karl-Friedrich Arndt, Technische Universität Dresden ,
Macromolecular Materials and Engineering, 2006

Model light-responsive
nanopatterned hydrogels

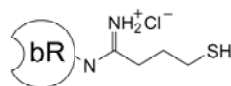
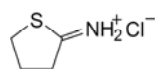


Synthesis of Poly (acrylic acid)-Bacteriorhodopsin Conjugate

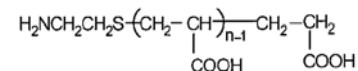
[bR with lysine K129]



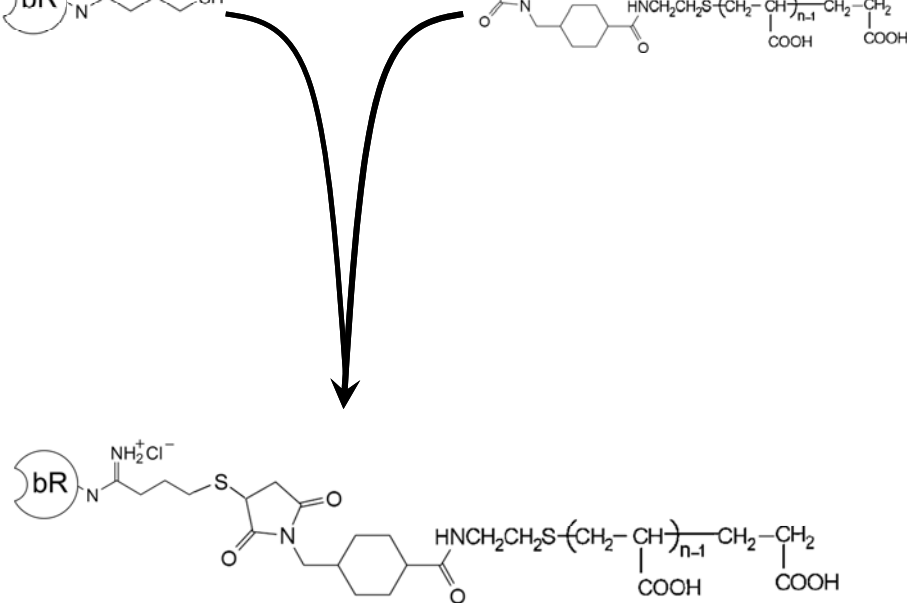
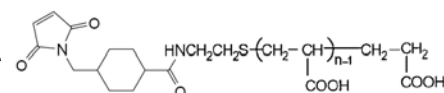
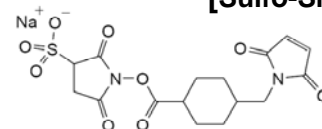
[Traut's Reagent]



[PAA-a]

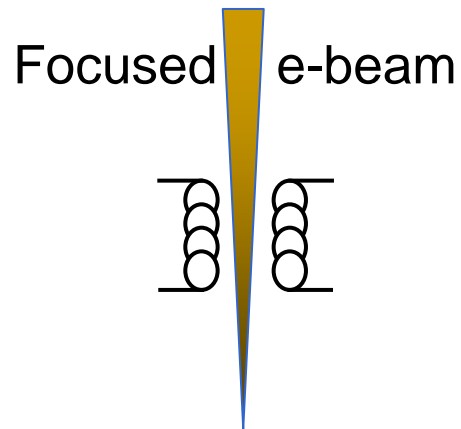


[Sulfo-SMCC]



[PAA-bR]

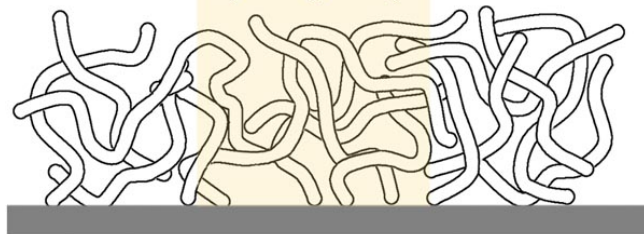
Electron Beam Patterning of Polymer Thin Film



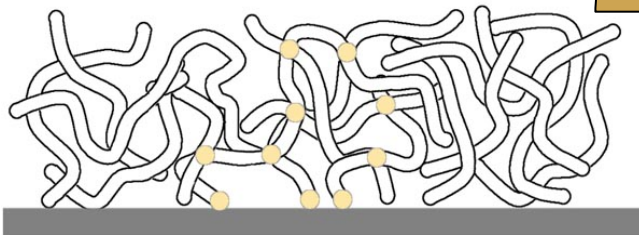
FEI XL30 SEM-FEG



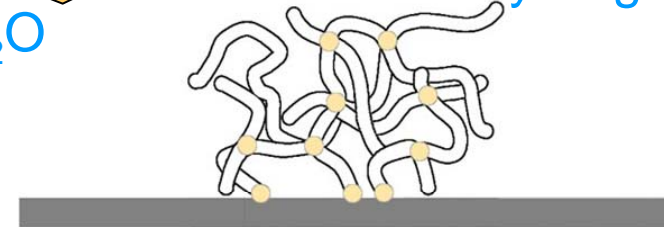
Spincoated thin polymer film



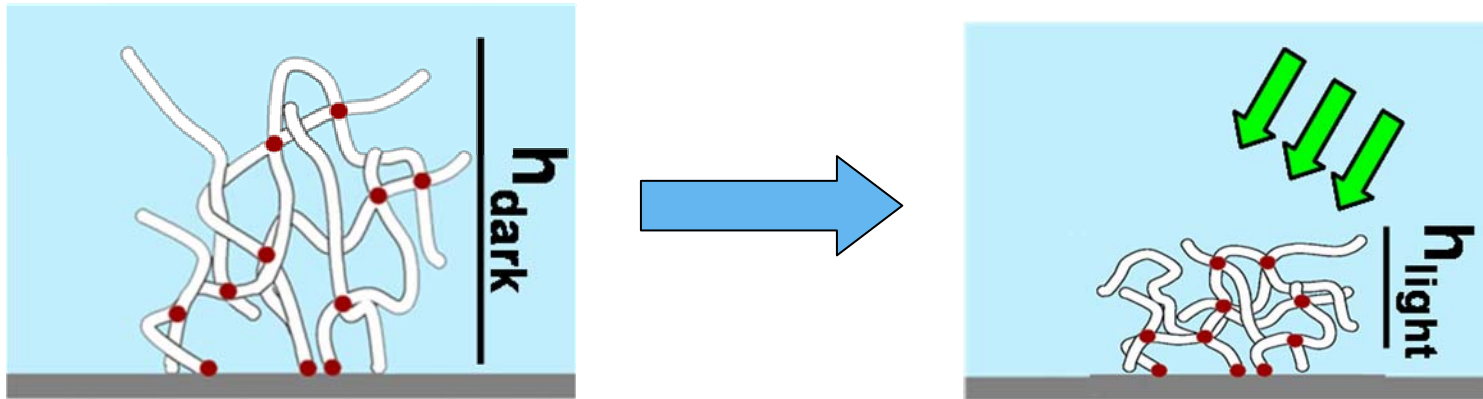
Develop in H₂O



Crosslinked hydrogel



What we expect to see



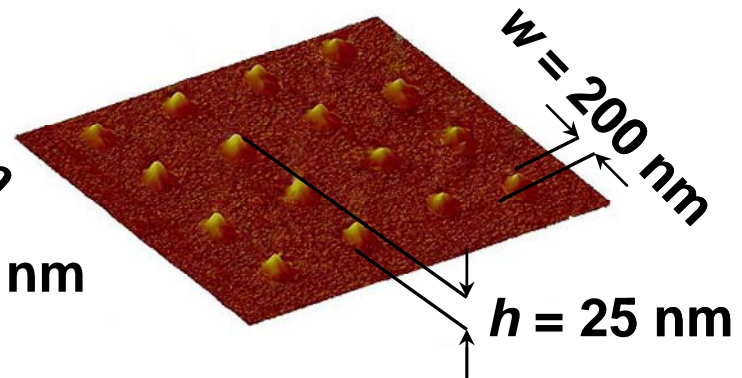
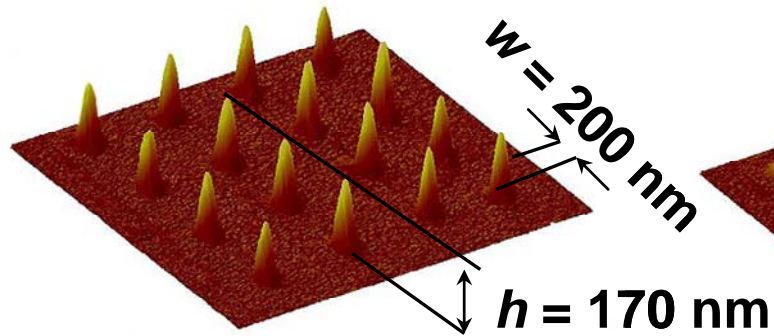
On exposure to visible green light

What the data looks like...

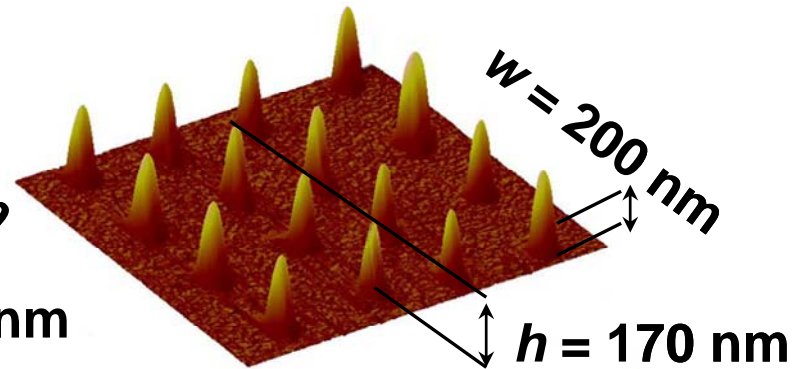
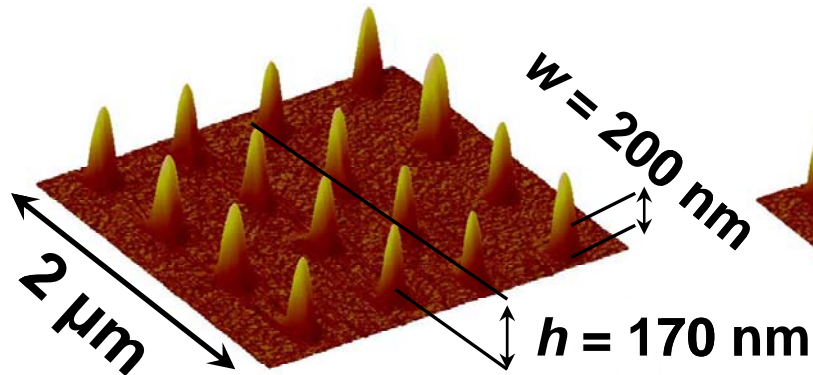
DARK

LIGHT

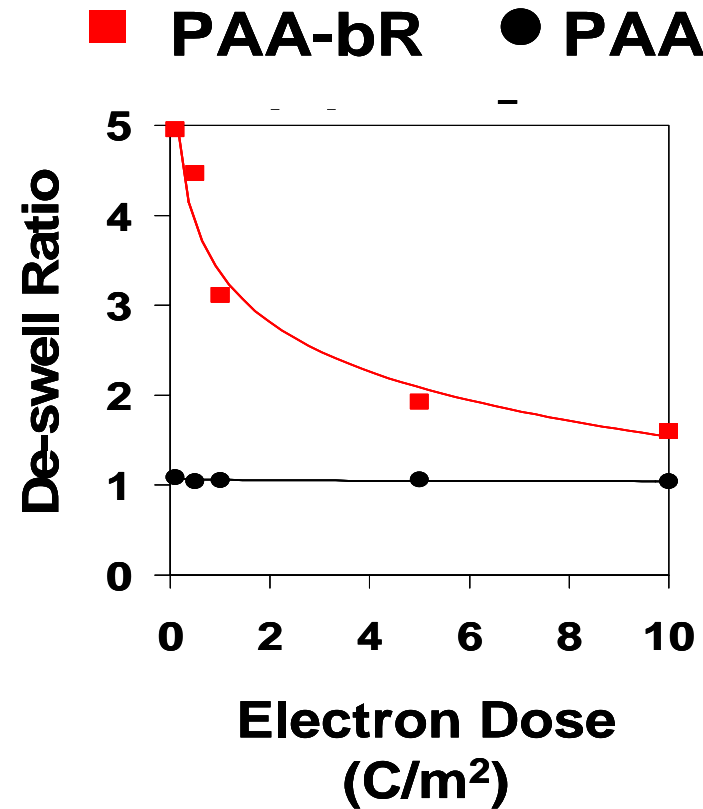
With
bR



Without
bR



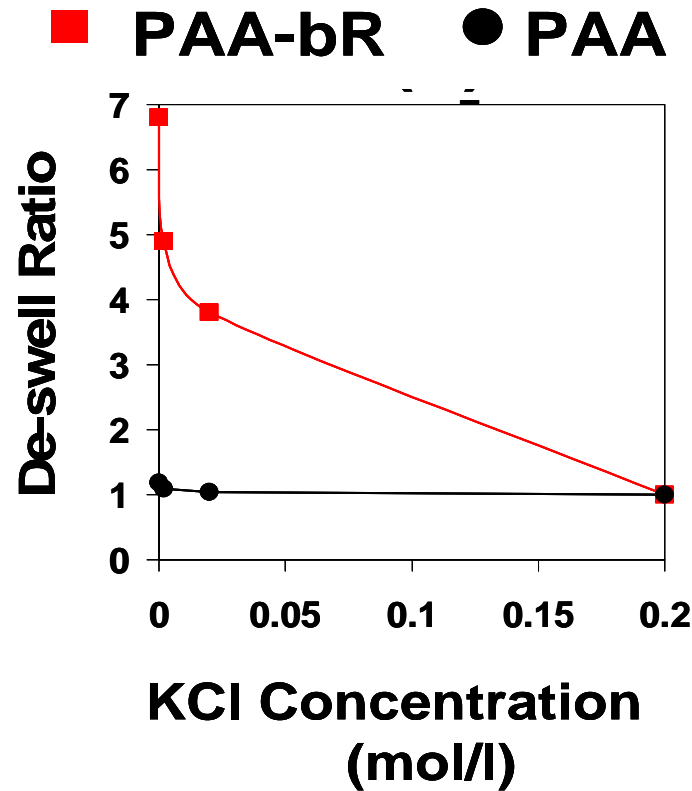
Response depends on electron-dose



Response displacement is dampened by:

- Electron dosage used for hydrogel fabrication

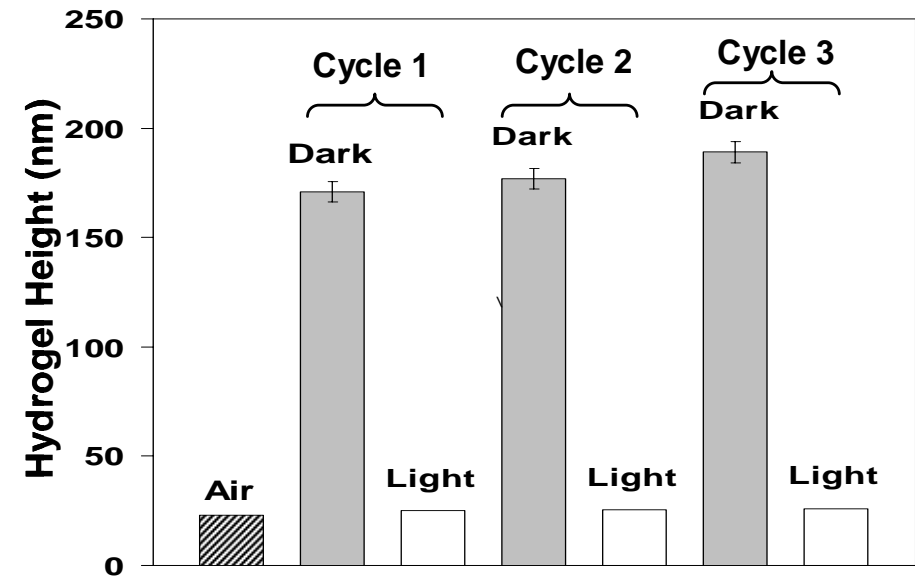
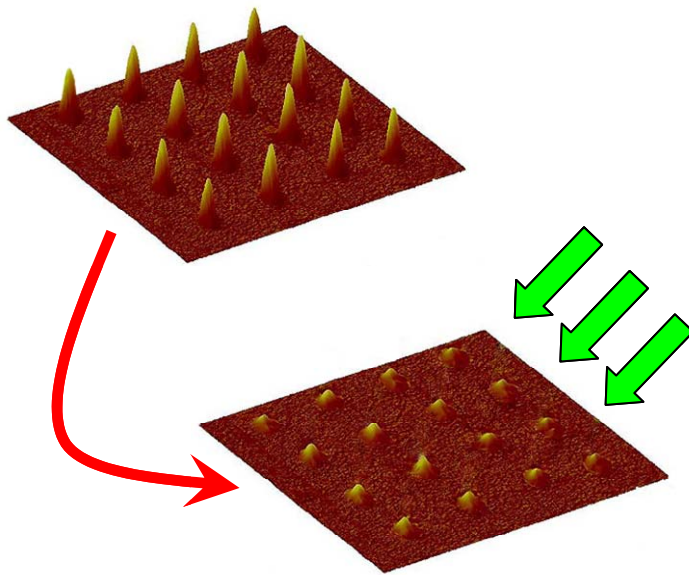
Response also depends on ionic conditions



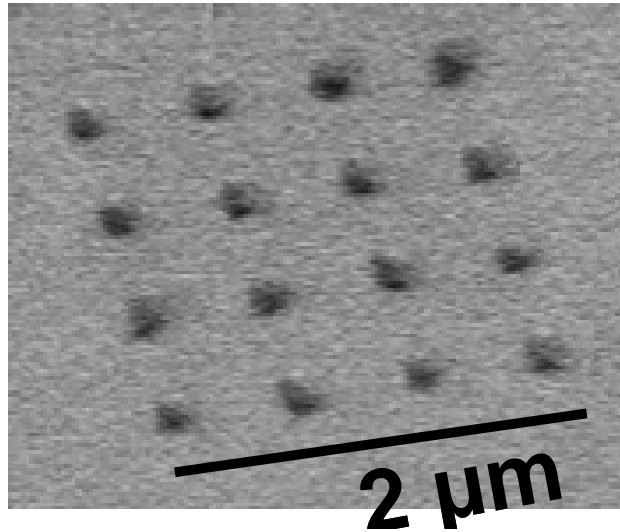
Response displacement is also dampened by:

- Salt concentration of environment

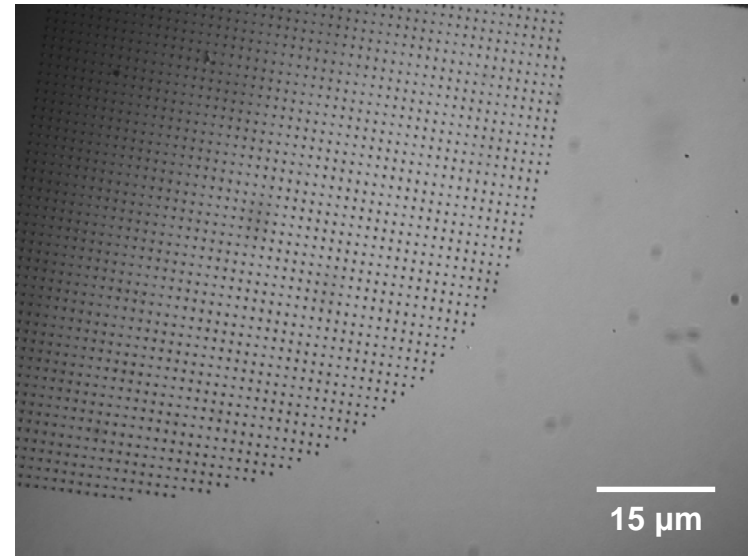
Response is repeatable under cyclic light/dark exposure



Arbitrary patterning of PAA-bR Hydrogels



SEM image of a 4x4
hydrogel dot array



Optical image of a large
array with a diameter of
100 μm

Conclusions

- Bacteriorhodopsin-containing hydrogels can be nanopatterned via e-beam and are responsive to visible green light
- Response characteristics are determined by electron-dose used in patterning, as well as environmental ionic strength
- Response is repeatable and arbitrary patterns can be formed

Acknowledgements

- Shared Materials Instrumentation Facility (Duke)
- Dr. Stefan Zauscher

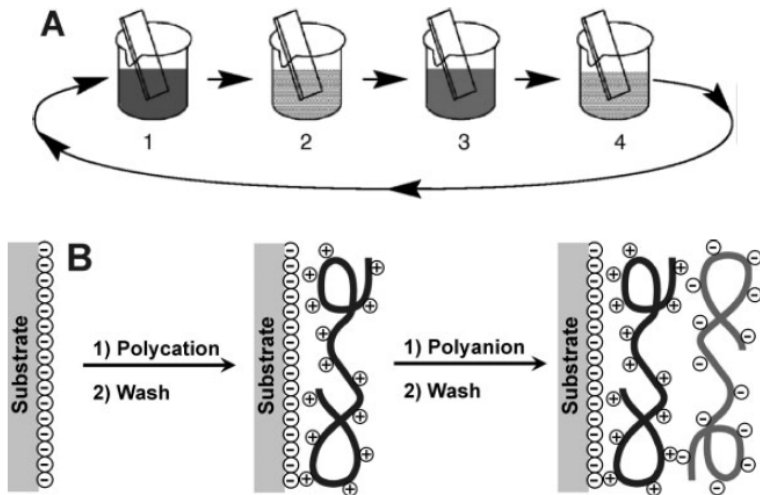
Tian Lab

- Dr. Kuo-sheng Ma
- Mr. Faisal Reza

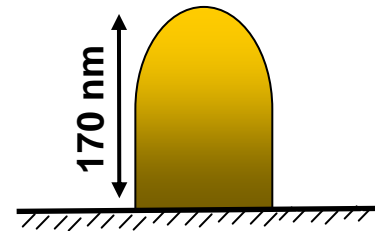
FUNDING:

- Beckman Foundation
- Hartwell Foundation
- Graduate Fellowship @ Duke BME
- Tau Beta Pi

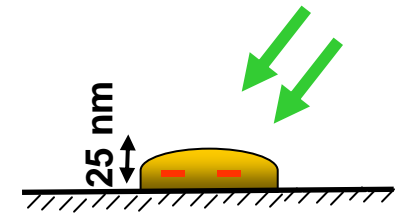
Layer-by-Layer Assembly



PAA is an anionic polyelectrolyte (-)

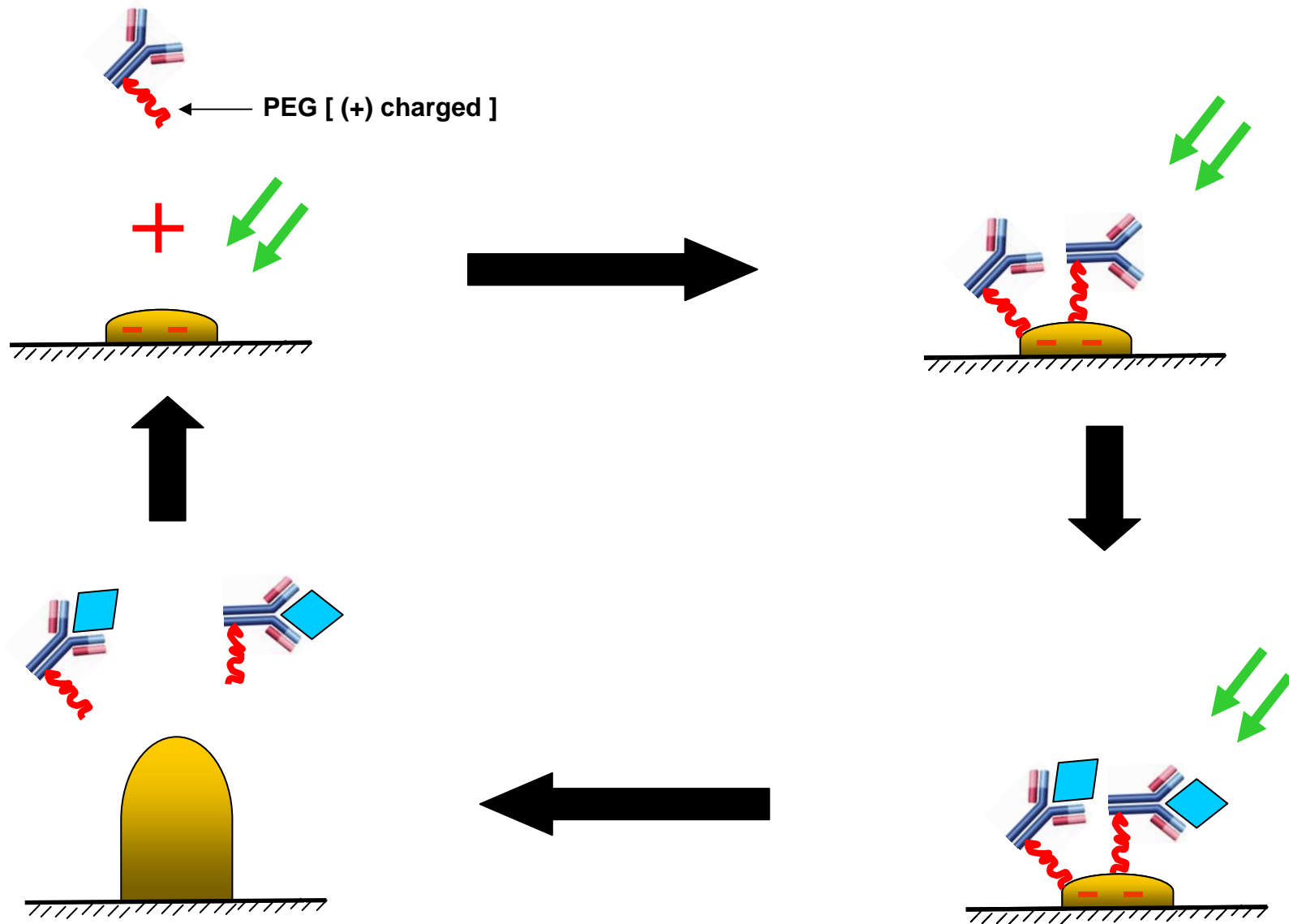


Neutral @
 $\text{pH} > \text{pK}_a [4.5]$

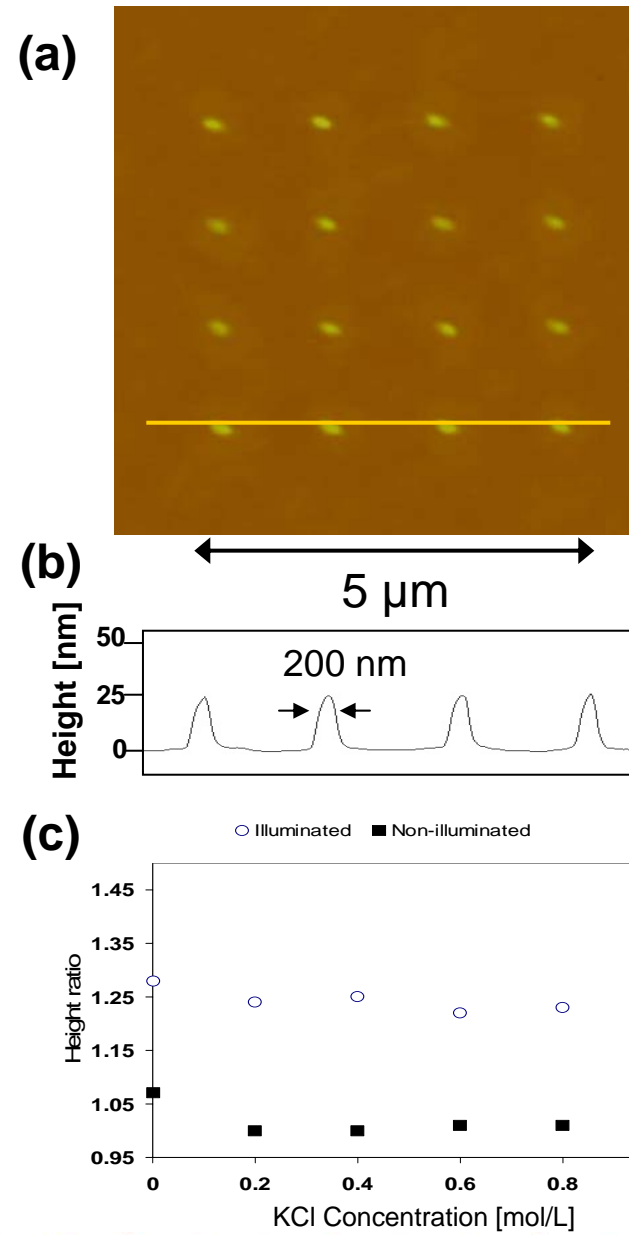


(-) charge @
 $\text{pH} < \text{pK}_a [4.5]$

Capture and Release from Nanopatterned Hydrogels

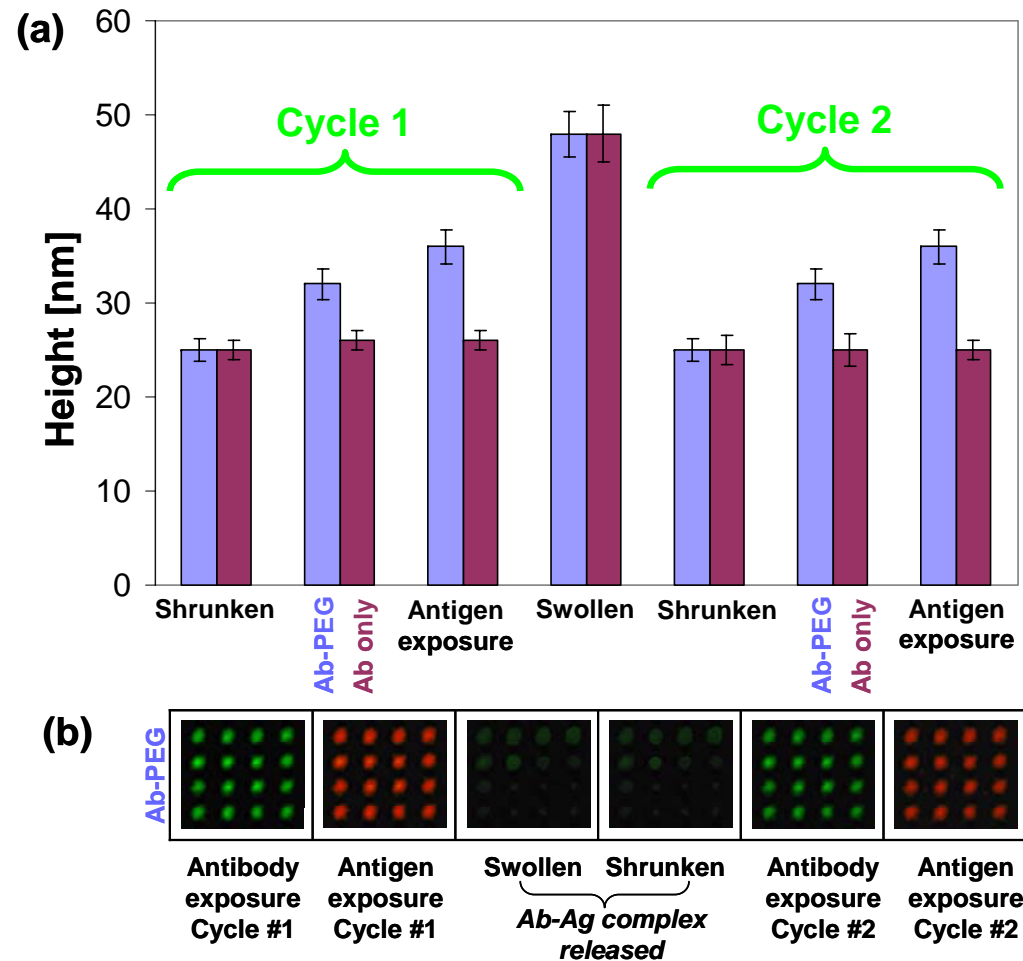


Ionic force do NOT influence capture

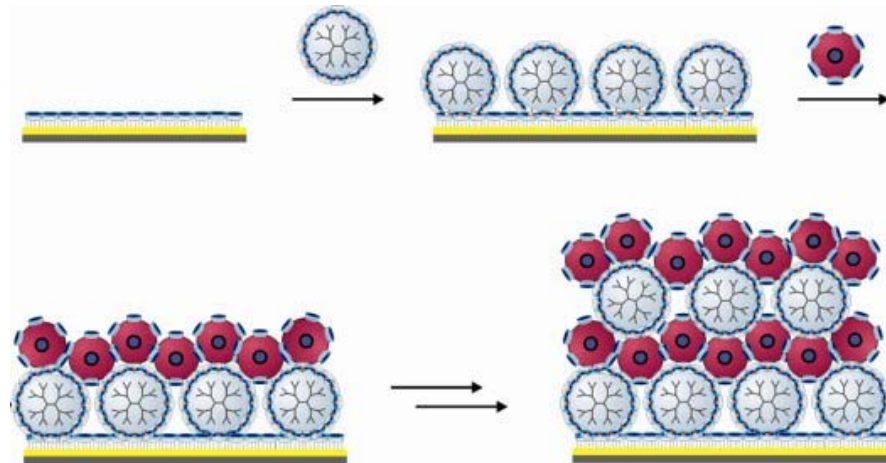


Reusable Protein Nanoarrays?

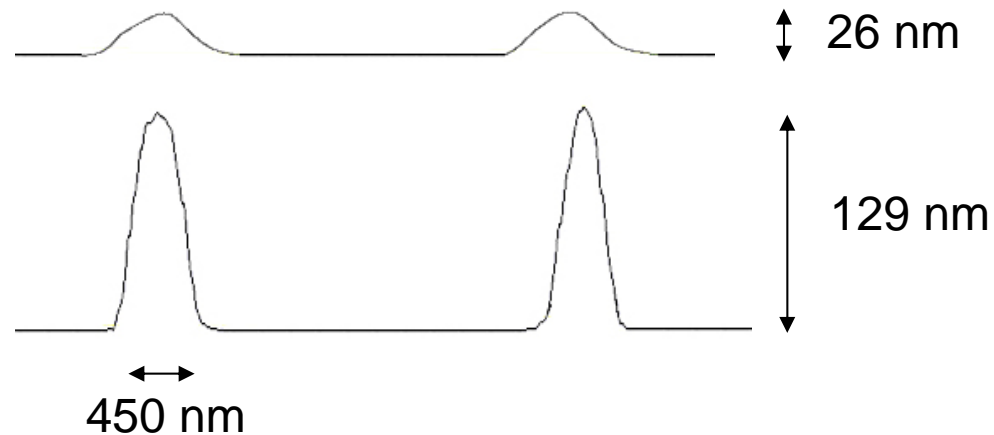
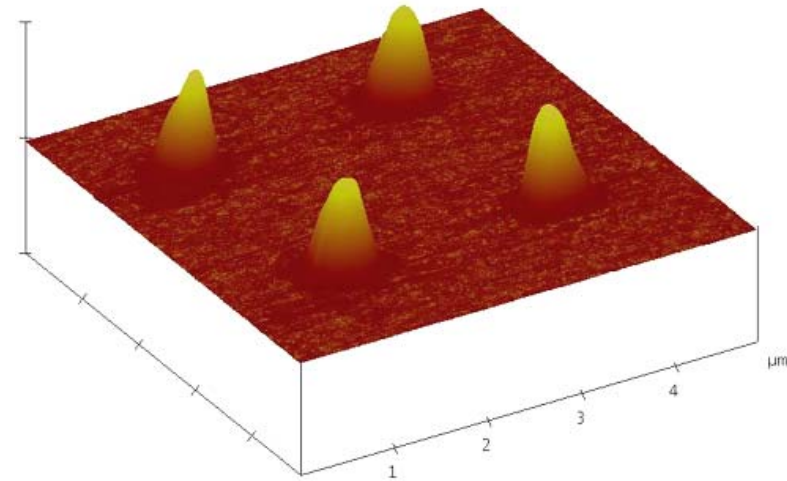
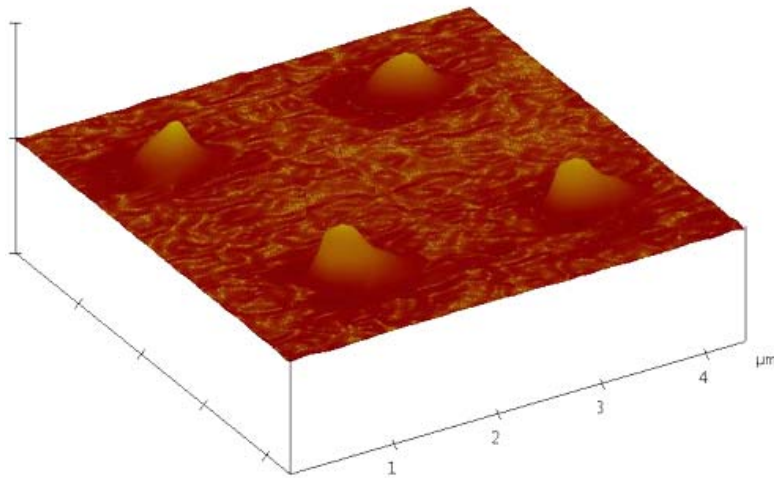
- Anti-GST with PEG-tag
- GST as antigen
- AFM analysis of height increase



Examples: Poly(acrylic acid) Actuators



Examples: Poly(acrylic acid) Actuators



Irradiated at 1 kV